

SODIUM NAPHTHALENE INDUCED REDUCTION AND SYMMETRIZATION OF ORGANOMERCURIALS

A PROJECT REPORT

Submitted to the

Department of Chemistry

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

as part of

the requirements for the Degree of

MASTER OF SCIENCE

by

BIDHU BHUSAN DAS

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

MAY, 1982

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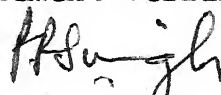
STATEMENT

I hereby declare that the work embodied in this report is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, under the supervision of Professor P.R. Singh.



Bidhu Bhusan Das

Statement Verified



(P.R. Singh)
Project Supervisor

3/5/82

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR, INDIA

CERTIFICATE

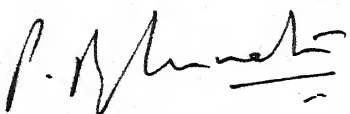
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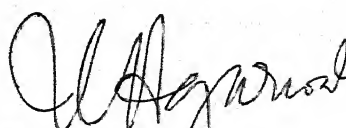
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Math	101	Mathematics I
Phy	101	General Physics I
TA	101	Engineering Graphics
Chm	102	General Chemistry II
Math	102	Mathematics II
Phy	102	General Physics II
TA	102	Introduction to Design
Chm	104	Experimental Method in Chemistry
H-Eng	111	English Language+Literature I
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Math	203	Mathematics III
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TA	203	Manufacturing processes I
Math	204	Mathematics IV
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ESc	211	Mechanics of Solids
ESc	221	Thermodynamics
H-Soc	222	Introductory Sociology
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It is my pleasant duty to record here my deep sense of gratitude to my project supervisor, Dr. P.R. Singh, Professor, Department of Chemistry, firstly for suggesting this challenging project and secondly for the many enlightening discussions we had during the course of this work. His constructive criticism and suggestions were always readily available to me and this has been a source of strength throughout.

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Finally, I thank all my friends in the campus for making my stay here a memorable one.

IIT-Kanpur
April 26, 1982.

Bidhu Bhusan Das

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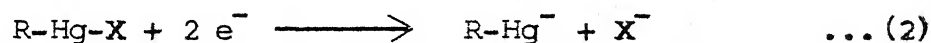
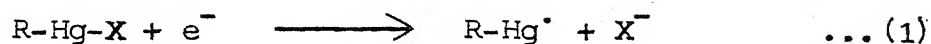
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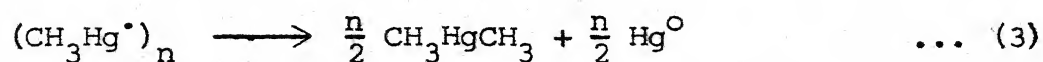
INTRODUCTION

Reduction of alkyl and arylmercuric salts can occur by one electron or two-electron transfer process as shown in Scheme I. The source of electrons may be a cathode, a metal, or another reducing agent.

SCHEME I

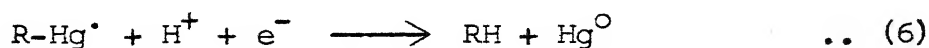
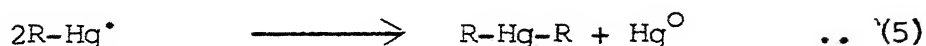
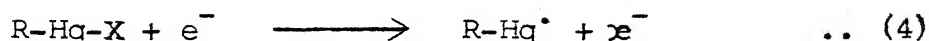


Kraus¹ demonstrated in 1913 that many alkyl mercuric halides can be reduced electrolytically. Methylmercuric chloride in liquid ammonia, for instance gives a dark, spongy, precipitate at the cathode. The exact nature of this precipitate which is a good electrical conductor remains in question today. It is perhaps best described as $(\text{CH}_3\text{Hg}^\bullet)_n$. Warmed to about room temperature, this material gives mercury and dimethylmercury in an exothermic reaction (Eqn. 3):



Related polarographic studies have been carried out by Benesch & Benesch,² on a number of alkylmercuric salts. The evidence supports the reaction shown in Scheme II,

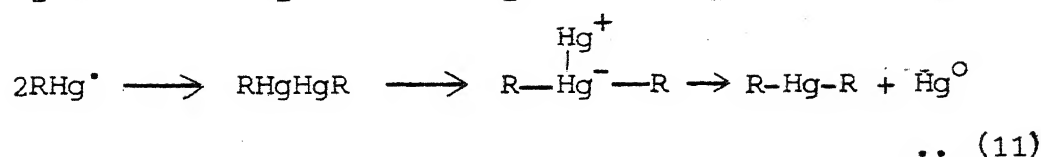
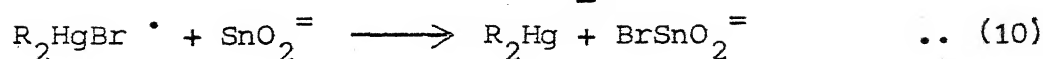
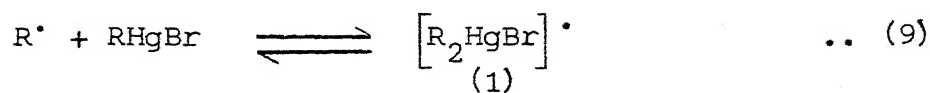
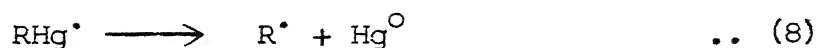
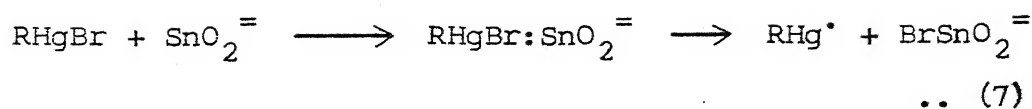
SCHEME II



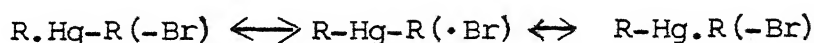
where the path taken by R-Hg^\bullet depends upon its concentration, the applied potential and the acid concentration.

Electropositive metals react with organomercurials by an oxidation-reduction process. The reduction usually proceeds to the dialkyl mercury compound and then more slowly to give the metal alkyl and more free mercury. The electropositive metals most commonly employed are sodium,^{3,4} copper,⁵⁻⁷ zinc,⁸ magnesium,⁹ and cadmium, copper and silver amalgams.¹⁰

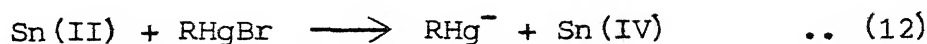
Sodium stannite¹¹⁻¹³ has been widely used as a reducing agent for mercurials and it gives excellent yield of products. The dialkyl compounds are generally stable to further reduction or they are reduced slowly. Traylor & Winstein¹⁴ have examined the stereochemical course of the sodium stannite symmetrization of several alkylmercuric halides. The evidence obtained by them leads to the mechanism shown in Scheme III.

SCHEME III

The structure of the intermediate (1) has been postulated as a resonance hybrid,

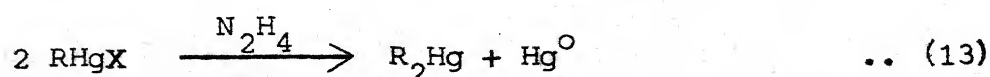


The mechanism of reduction by stannite in Scheme III could be accompanied by a substantial amount of a two-electron transfer reaction,

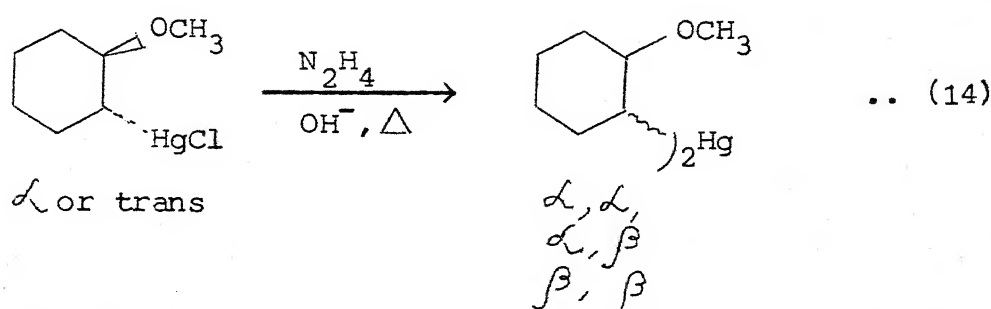


and still show the observed effects.

Gilman and Wright¹⁵ were the first to note the formation of diorganomercurials on treatment of an organomercuric halide with hydrazine (Eqn. 13):

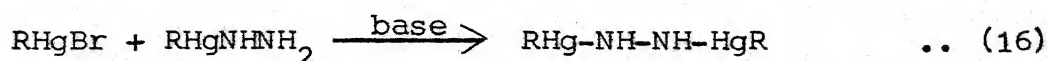
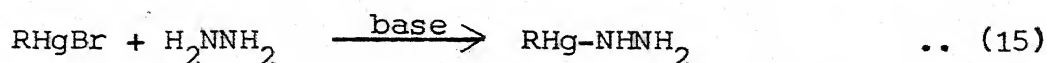


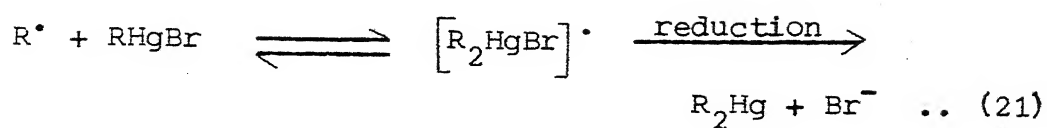
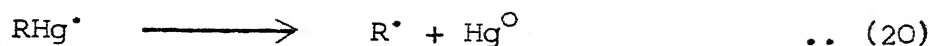
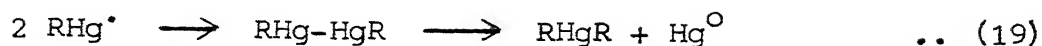
Subsequently, it has been established that prolonged treatment causes further reduction with concurrent formation of hydrocarbon and olefinic products.³⁶ This important work also established that treatment of a single diastereomer of 2-methoxycyclohexylmercuric chloride with hydrazine gives rise to a mixture of diastereomeric dialkyl mercury products (Eqn.14):



Racemization and formation of diorganomercurial from 2-methoxycyclohexylmercuric halide (reduction by magnesium, which is believed to be a two-electron transfer, yields only olefin) are considered indications of a one-electron transfer reaction for hydrazine. However, hydrazine alone reduces alkylmercuric halides very slowly, whereas the reaction proceeds rapidly in the presence of alkali, suggesting an (at least partially) ionic mechanisms. To account for these observations the mechanism given in Scheme IV has been postulated.

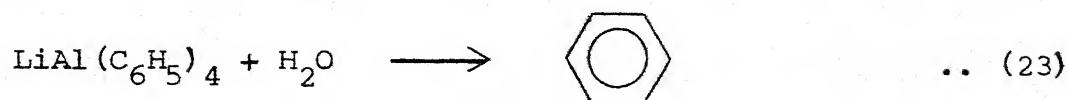
SCHEME IV



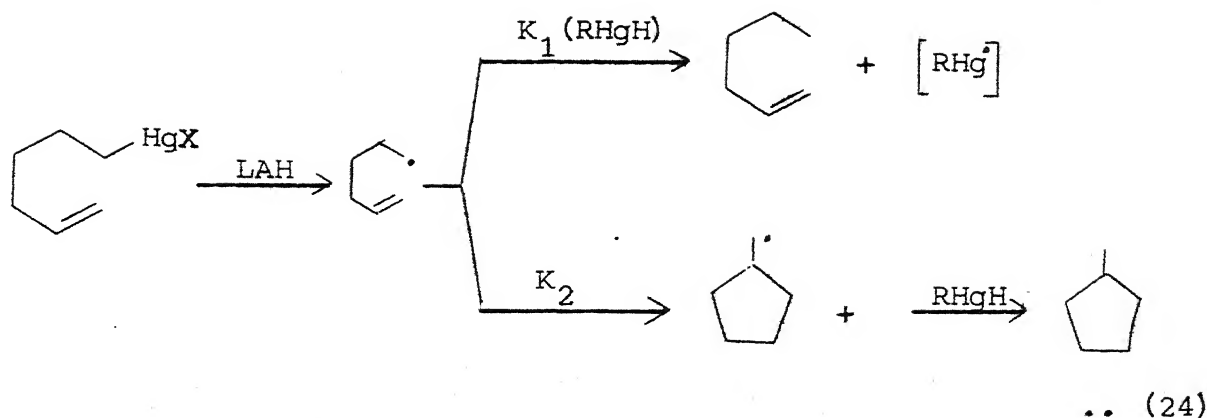


Here, the function of base is to form RHg-NHNH_2 or RHg-NHNH-HgR , followed by homolytic cleavage to form RHg^\bullet and diimide.

Winstein and Traylor¹⁷ demonstrated that lithium aluminium hydride reduces alkyl and aryl mercuric halides to the hydrocarbon. Traylor¹⁸ postulated that an intermediate organoaluminium compound is formed in these reactions, which on hydrolysis yields the hydrocarbon.

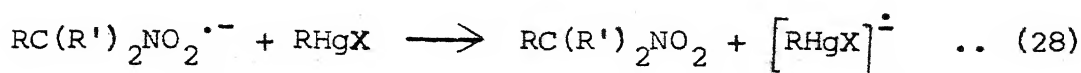
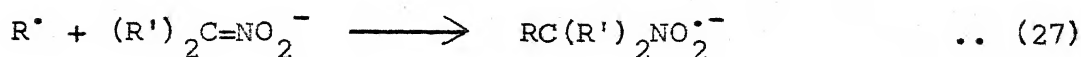
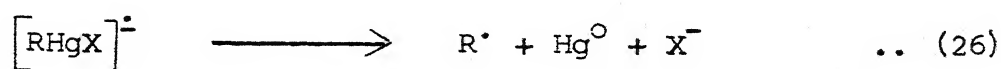


Free radical intermediates have also been proposed in the reaction of alkylmercuric halides with LAH ¹⁹ (Eqn. 24):



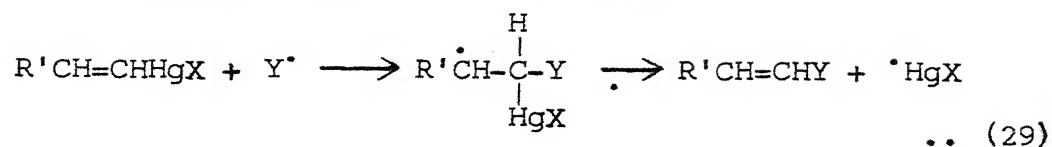
Recently Russel and coworkers have demonstrated that alkylmercuric halides participate in the $S_{RN}1$ reaction with nitronate anions²⁰ in Me_2SO or DMF (Scheme V):

SCHEME V

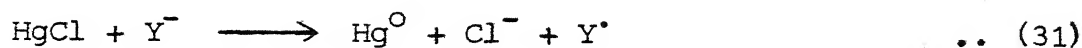


This reaction is inhibited by di-tert-butyl nitroxide (a known radical scavenger) and was catalysed by light. Vinylmercurials fail to participate in a chain reaction with nitronate anions. However, vinylmercurials do give a radical chain substitution reactions²¹ with anions such as $Y^- = RS^-$, RSO_2^- , $(RO)_2PO^-$, or $ROP(R')O^-$. According to Russel these reactions

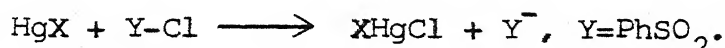
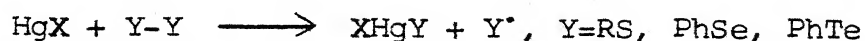
involve an addition elimination mechanism:



The chain is apparently propagated by reaction of HgX such as:



Vinylmercurials also undergo free radical chain substitution with RSSR, PhSeSePh, PhTeTePh or PhSO₂Cl. In these cases²² the addition elimination reaction is followed by propagation steps such as:

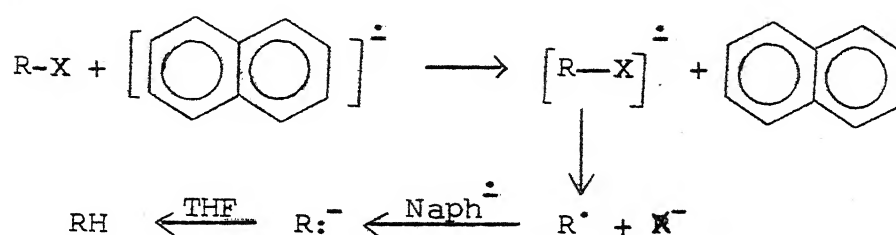


All these reactions are photostimulated and are inhibited by radical scavengers.

Radical anions derived from aromatic hydrocarbons by the reaction with alkali metals serve as excellent sources of electrons in many well studied electron transfer reactions.^{23,24} Of all the aromatic hydrocarbon radical anions the naphthalene radical anion has been studied best.²⁵⁻²⁸

The most common role of the naphthalene radical-anion ($\text{Naph}^{\cdot-}$) i.e., as an electron transferring agent, is illustrated in Scheme VI where RX is assumed to be an electron acceptor with X as a leaving group and R as an aliphatic or aromatic group.

SCHEME VI



The reduction of the initially formed radical to the corresponding carbanion has been confirmed by trapping the latter in the form of the Grignard reagent using MgBr_2 .²⁹⁻³¹

In view of the known electron accepting characteristic of alkyl and arylmercuric halides and the known electron donating nature of the naphthalene radical-anion, it was considered worthwhile to examine the reduction and symmetrization of a few alkyl and aryl mercuric halides with sodium naphthalene, with a view to determine the reaction pathway involved.

EXPERIMENTAL

All melting points were recorded on a Mel-Temp melting point apparatus and are uncorrected. Silica gel (Acme's) was used for thin layer chromatography (TLC) and silica gel (Acme's) of 100-200 mesh was used for all chromatographic separations. The GLC analyses were carried out on chromatography and Instrument Company, Baroda, Chromatography model AC1-FI using 15% SE-30 on Cromp-P (100-120M) column of 2 m length.

Tetrahydrofuran was purified by keeping it over potassium hydroxide pellets overnight, refluxing over sodium wire for 5-6 hours and distilling over sodium. It was stored in contact with freshly drawn sodium wire. Reagent grade naphthalene (BDH) was recrystallized from ethanol. Benzyl and phenylmercuric chlorides were prepared by the reaction of mercuric

chloride with the respective magnesium chlorides.¹ Authentic samples of benzene (BDH) and toluene (BDH) were used after distillation.

Preparation of Sodium Naphthalene²

In a three necked flask mounted on a magnetic stirring base, fitted with a device to pass pure and dry nitrogen, a dropping funnel and connected to a mercury trap, naphthalene (1.28 g, 0.01 mol) dissolved in dry THF (50 ml) was taken. The contents of the flask were 20°C. Magnetic stirring was started and dry nitrogen gas was passed through the solution for 30 minutes. Sodium metal (0.36 g, 0.015 g.atom) cut into small pieces was added to it. The mixture was stirred rapidly in the beginning and slowly after the reaction had started. The progress of the reaction was measured from time to time by removal of a small sample of solution from the reaction mixture and determination of its sodium content after dilution with alcohol, by titration with standard hydrochloric acid using methylred as indicator. The reaction was found to be complete in about 3 hours.

(I) Reaction of Benzyl mercuric chloride with Sodium naphthalene at room temperature (30°C)

(a) With equimolar (0.01 mole) ratio of reactants under nitrogen atmosphere for 30 minutes

In a three-necked 250 ml round bottom flask mounted on a magnetic stirrer base and connected with a gas passing

adapter and a mercury trap, a slurry of benzyl mercuric chloride (3.27 g, 0.01 mol) in 50 ml THF was taken at room temperature (30°C). Pure dry nitrogen gas was passed through the solution for 30 minutes under continuous stirring. The sodium naphthalene solution (0.01 mol) contained in 50 ml of THF was added gently through a pressure equalizing dropping funnel. The mixture was stirred for 30 minutes. Mercury precipitated in a greenish grey form was removed by filtration through celite after quenching of the reaction mixture with 100 ml of 2% hydrochloric acid. The filtrate was extracted with diethyl ether (6 x 75 ml) and the combined extract was washed with water and dried over anhydrous Na_2SO_4 . After filtration, ether solvent was evaporated carefully at room temperature under reduced pressure. The mixture was concentrated to a volume of approximately 50 ml and then analysed by GLC using a 15% SE-30 on Crom-P (100-120 M) column of 2 m length. The yield of toluene 2% and bibenzyl 25% was obtained by comparison of the retention times and peak areas with those of authentic samples. The solvent was then evaporated off and the solid so obtained was shaken vigorously with petroleum ether (b.p. 60-66°C). The petroleum ether insoluble portion was filtered and identified as benzyl mercuric chloride (2.22 g, 68%). The material obtained after removal of petroleum ether from the filtrate was chromatographed over silica gel column using petroleum ether (b.p. 60-80°C) as eluant. The products thus obtained

were: naphthalene (1.088 g, 85%), bibenzyl (~ 0.20 g, 22%) and dibenzyl mercury (~ 0.1 g, 5%). The compounds were characterized by comparison of IR spectra, mixed melting points and thin layer chromatography.

(b) With equimolar (0.01 mol) ratio of reactants under nitrogen atmosphere for 360 minutes

Reaction I(a) was repeated and stirring was carried out continuously for six hours. The product distribution determined in the same way was: benzyl mercuric chloride (2.03 g, 62%); toluene (5%); bibenzyl (27%); bibenzyl mercury (~ 0.1 g, 5%); and naphthalene (1.087g, 85%).

(c) With benzyl mercuric chloride (0.01 mol) and sodium naphthalene in 1:2 molar ratio under nitrogen atmosphere for 30 minutes

Benzyl mercuric chloride (3.27 g, 0.01 mol) in THF (50 ml) was allowed to react with sodium naphthalene (0.02 mol) contained in 50 ml of THF under otherwise identical conditions to those of experiment I(a). The reaction mixture was worked up as usual and product distribution was found to be: benzyl mercuric chloride (~ 0.326 g, 70%); toluene (30%); bibenzyl (53%); dibenzyl mercury (trace); and naphthalene (~ 2.30 g, 90%).

(II) Reaction of Phenyl mercuric chloride with Sodium naphthalene at room temperature (30°C).

(a) With equimolar (0.01 mol) ratio of reactants under nitrogen atmosphere for 30 minutes

The reaction of phenylmercuric chloride (3.125 g, 0.01 mol) in dry, THF (50 ml) was carried out by adding to it a 50 ml solution of sodium naphthalene (0.01 mol) under nitrogen atmosphere at room temperature (30°C) for 30 minutes as in Experiment I(a). Mercury precipitated in a greenish grey form, which was removed by filtration through celite after quenching of the reaction mixture with 100 ml of 2% hydrochloric acid. The product distribution obtained was phenyl mercuric chloride, (~1.41 g, 45%); benzene (10%); biphenyl (~5%); diphenyl mercury (0.62 g, 35%); and naphthalene (~1.2 g, 90%).

(b) With equimolar (0.01 mol) ratio of reactants under nitrogen atmosphere for 720 minutes

The above reaction II(a) was repeated under identical conditions but continued for 12 hours and worked up as in experiment I(a). The product distribution found in this reaction was: phenyl mercuric chloride (1.13 g, 36%); benzene (13%); biphenyl (~5%); diphenyl mercury (0.71 g, 40%); and naphthalene (~1.2 g, 90%).

(c) With phenyl mercuric chloride (0.01 mol) and sodium naphthalene in 1:2 molar ratio under nitrogen atmosphere for 30 minutes

A solution of sodium naphthalene (0.02 mol) in 50 ml THF was added to the solution of phenyl mercuric chloride (3.125 g,

0.01 mol) and reaction continued under nitrogen atmosphere for 30 minutes under similar conditions as described under Experiment II(a). The reaction mixture was worked up as in Experiment II(a). The product distribution was phenylmercuric chloride (0.31 g, 10%); benzene (35%); biphenyl (~5%); diphenyl mercury (0.8 g, 45%); and naphthalene (2.2 g, 87%).

(III) Reaction of Sodium naphthalene with Benzyl mercuric chloride in presence of MgBr_2 . Trapping of benzyl anion

(a) Preparation of MgBr_2 : Magnesium (0.48 g, 0.02 g.atm) and THF (25 ml) were taken in a three-necked flask which was equipped with a magnetic stirring device, a gas passing adapter, a condenser and a pressure equalizing dropping funnel. The contents were kept under N_2 atmosphere and 1,2-dibromoethane (3.8 g, 0.02 mol) was slowly added with the help of the dropping funnel. Stirring was continued for an hour during which period MgBr_2 precipitated out.

(b) A solution of benzyl mercuric chloride (3.27 g, 0.01 mol) in THF (30 ml) was added to the flask containing MgBr_2 . Reaction was carried out with sodium naphthalene (0.01 mol) contained in THF (50 ml) as usual, at room temperature and the contents of the flask stirred for 15 min, after which a solution of benzophenone (1.8 g, 0.01 mol) in 20 ml THF was added. The contents of the flask were stirred for 4 hour at room

temperature. The mixture was then poured into 100 ml, 2% hydrochloric acid and was worked up as usual. TLC analysis of the product mixture did not give any spot for benzyl diphenyl carbinol.

DISCUSSION

Reactions of two mercuric salts namely: benzyl mercuric chloride (I), and phenyl mercuric chloride (II) with equimolar quantities of sodium naphthalene in THF under nitrogen atmosphere and at room temperature (30°C) for 30 minutes were largely incomplete and unreacted mercuric halides recovered were: I(68%), and II(45%). On extending the reaction time more mercuric halide reacted in both the cases; but even then, a large amount of the mercuric halide was recovered unchanged. Mercuric halides (I) and (II) were, therefore, reacted with double the quantity of sodium naphthalene under the same conditions for 30 minutes. Under these conditions the reaction with both the mercuric halides was almost complete in 30 minutes. The results of our experiments on mercuric halides (I) and (II) are summarized in Table 1.

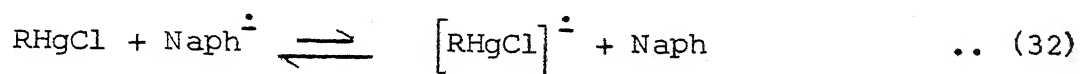
TABLE 1

Reduction of Organomercurial Halides by Sodium Naphthalene

Reaction of benzylmercuric chloride and phenylmercuric chloride (0.01 mol) with sodium naphthalene, in THF at room temperature (30°C), under nitrogen atmosphere.

Sl. No.	R-Hg-Cl	Molar ratio RHgCl/Naph	Reaction Time	% Yield of Products				
				R-H	R-R	R-Hg-R	Naph ^a	R-Hg-Cl
1.	Benzylmercuric chloride	1:1	30 min.	2	25	~5	85	68
2.	"	1:1	360 min.	5	27	~5	85	62
3.	"	1:2	30 min.	30	53	trace	90	10
4.	Phenylmercuric chloride	1:1	30 min.	10	~5	35	90	45
5.	"	1:1	720 min.	13	~5	40	90	36
6.	"	1:2	30 min.	35	~5	45	87	10

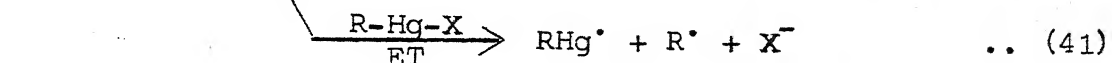
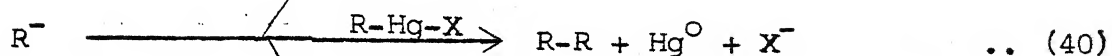
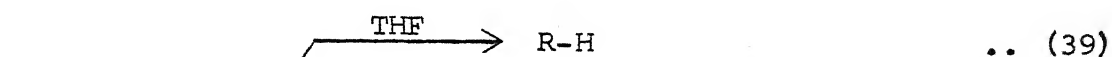
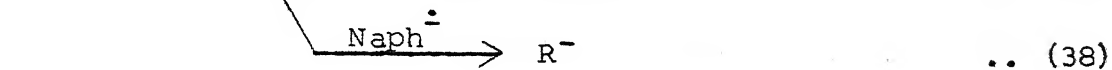
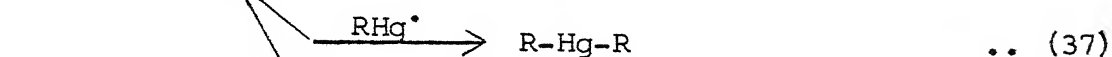
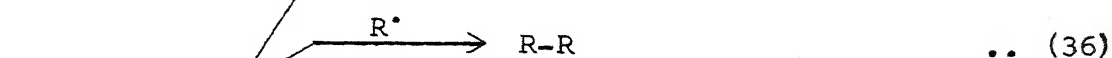
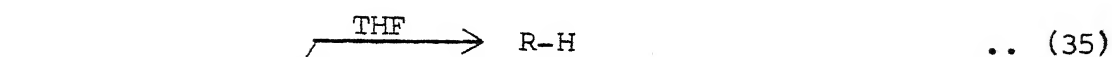
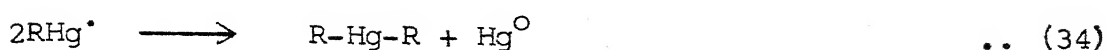
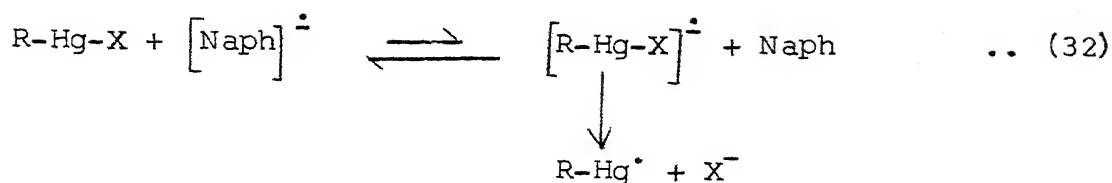
The results of experiments with 1:1 molar ratios indicate that an excess of sodium naphthalene is required not so much for starting the reactions as for forcing these towards completion. It is likely that an equilibrium of the type shown in Eqn. (32) is set up on mixing the reactants. This equilibrium is far towards the left in presence of lower concentration of the electron donor:



In presence of a large excess of the electron donor, however, the equilibrium shifts towards the right side giving high concentration of the mercuric halide radical anion. The electron transfer from sodium naphthalene to phenyl mercuric halide is reversible was established by carrying out a reaction with the addition of 200 mol % excess of neutral naphthalene to the phenyl mercuric halide (0.005 mol) initially and then reacting it with equimolar quantity of sodium naphthalene. Under these conditions, 65% of (II) was recovered unchanged after 30 min.

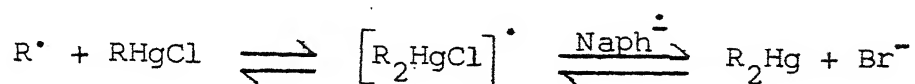
Isolation of diorganomercurials R-Hg-R, and dimers R-R coupled with the precipitation of metallic mercury in our experiments leads us the more probable mechanistic pathway outlined in Scheme VII:

SCHEME VII



The bond dissociation energy of RHg^{\cdot} , where $\text{R} = \text{alkyl}$, is very small³² varying from 0-6 kcal/mol. Therefore the decomposition of $\text{C}_6\text{H}_5\text{CH}_2\text{Hg}^{\cdot}$ at room temperature can be expected to be very rapid as shown in Eqn. (34). Thus only a small amount of dibenzyl mercury is obtained and the major reaction product is bibenzyl, formed by the coupling of benzyl radicals. In the reaction with phenylmercuric chloride, the PhHg^{\cdot}

radicals formed are quite stable due to the resonance stabilization of the odd electron on mercury. Thus the decomposition of PhHg^\bullet is not very fast and the major product obtained is diphenylmercury, Ph-Hg-Ph . Diorganomercurials may also be obtained by reduction of the hypothetical adduct formed between radicals and the organomercuric halide.³³



Both phenyl and benzyl radicals would accept an extra electron from sodium naphthalene, in our experiments with 1:2 molar ratio of the reactants, to give the corresponding anion³⁴ in a major way, as shown in Eqn. (38). These anions give the corresponding hydrocarbons by picking up protons either from THF or during work up. They may also attack the starting mercuric halides, yielding dimers or may also transfer an electron to the starting mercuric halide, as shown in Eqn. (40) and (41).

Reaction shown in Eqn. (38), considerably depletes the concentration of naphthalene radical anion reagent. But the formation of anions in our experiment with 1:1 molar ratio of the two reactants is not likely in view of the results of the control experiment conducted by us with benzylmercuric chloride.³⁰ Thus on reacting benzylmercuric chloride (0.01 mol) with sodium naphthalene (0.01 mol) in the presence of MgBr_2 and on subsequent reaction with benzophenone, no benzyl diphenyl carbinol

was obtained.

In conclusion, it is our opinion that an electron transfer mechanism of the type outlined in Scheme VII nearly explains our observations and represents the mechanism valid under our experimental conditions.

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VITAE

I was born at Silchar and after my early schooling in the suburb of Silchar, I passed the High School Leaving Certificate Examination from Adhar Chand High School, Silchar, under the Board of Secondary Education, Assam, Gauhati. Then after passing the P.U.Sc. Examination from G.C. College, Silchar of the University of Gauhati, Gauhati in July, 1976, I joined this Department for the degree of Integrated M.Sc. in July, 1976.

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